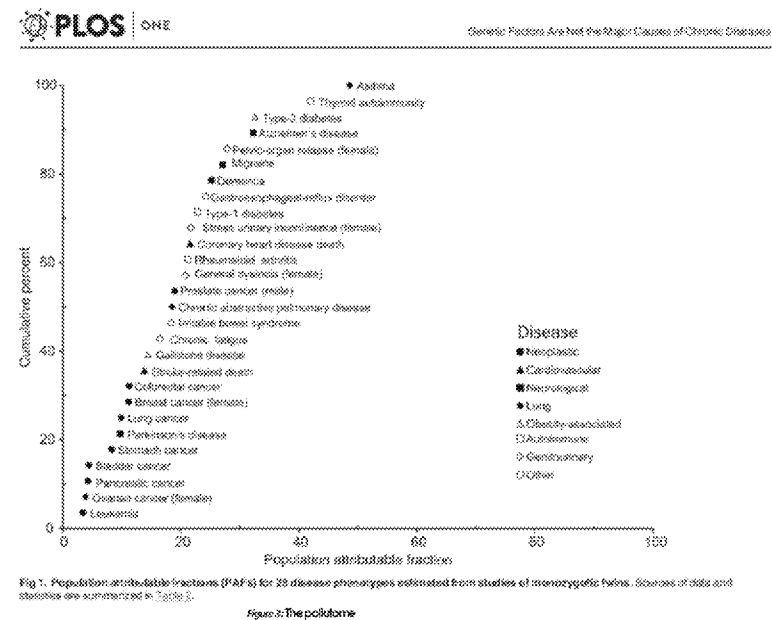
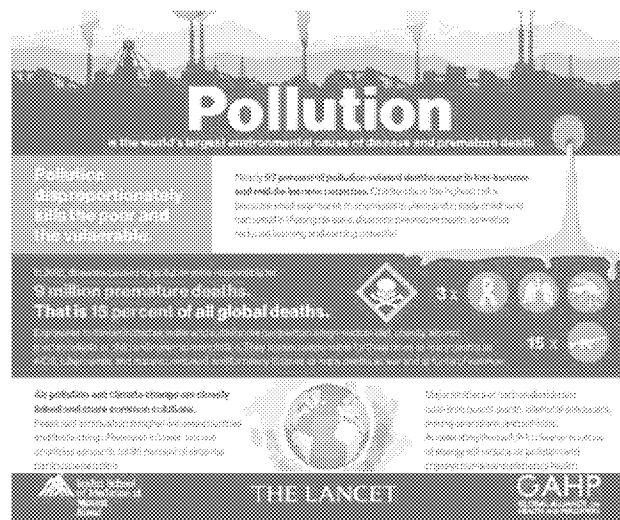


Broader Public Health Context

- Pollution is known to be a leading public health threat (Landrigan et al. 2017)
- A large proportion of the environment attributed disease is of unknown etiology (Rappaport, 2016)



Chemical Pollution

- Exposure and effects are poorly understood
- Effects likely underestimated
- Historical lessons – Pb, asbestos, DDT, PCBs
- Chemical production and release to the environment vastly out pace ability to test and measure

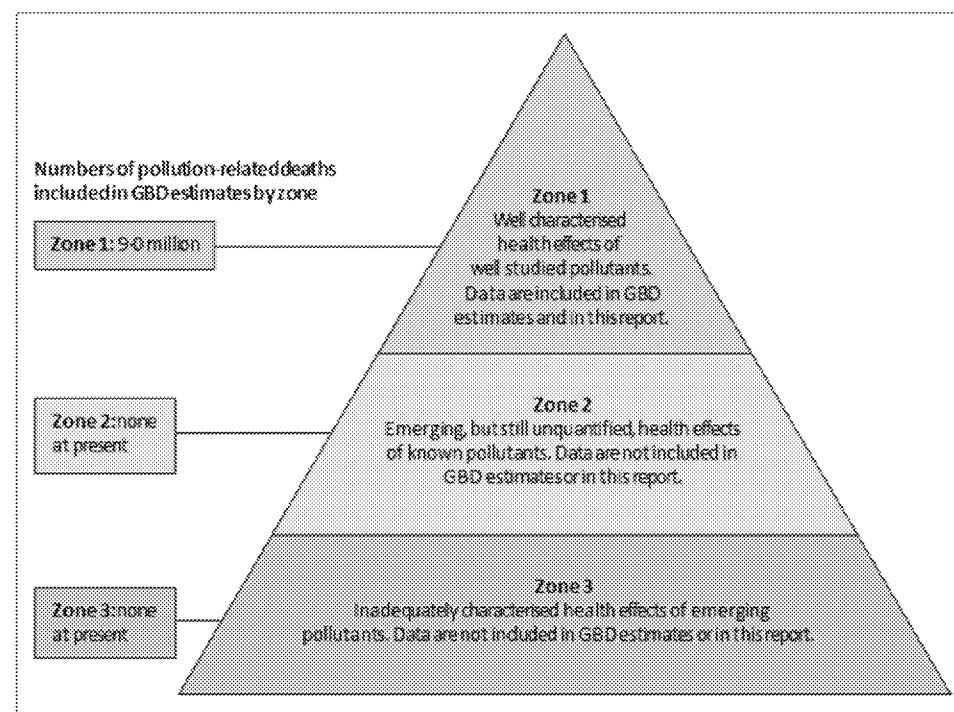
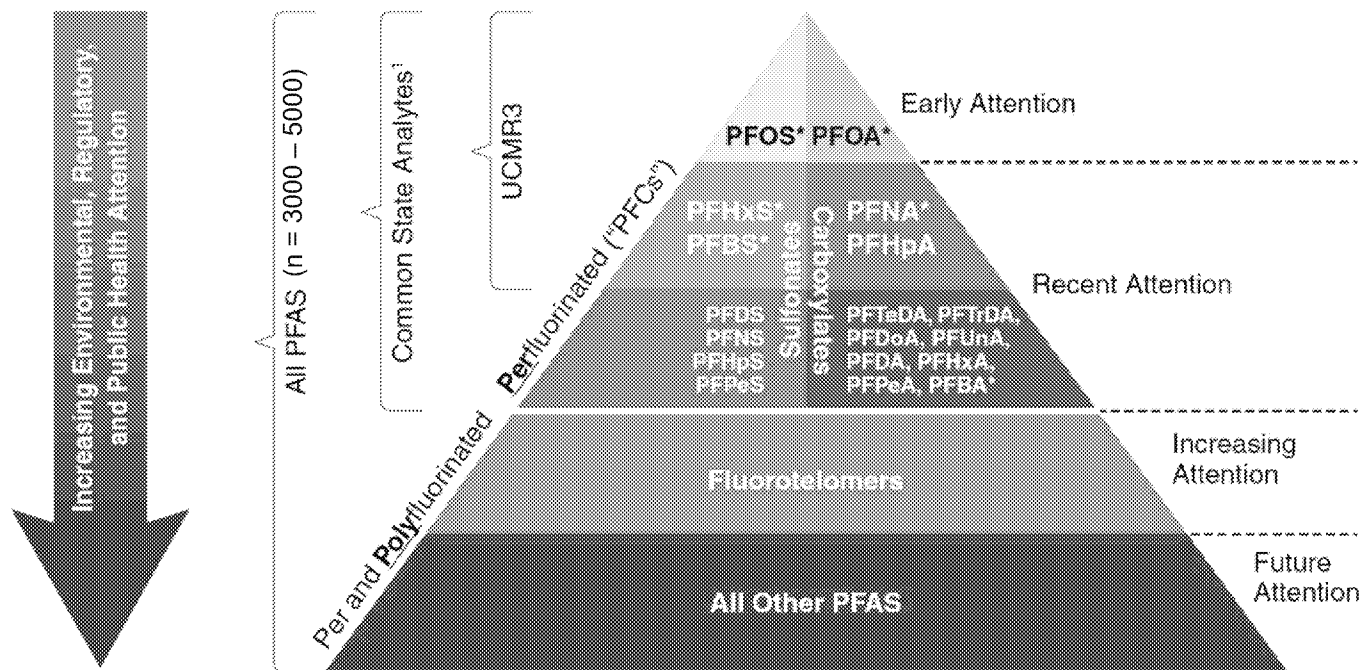
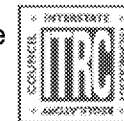


Figure 3: The pollutome

The Vast PFAS Unknown



Source

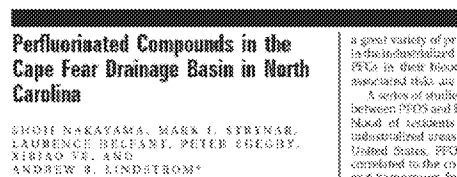


ITRC
50 F St. NW, Suite 350
Washington, DC 20001
itrcweb.org

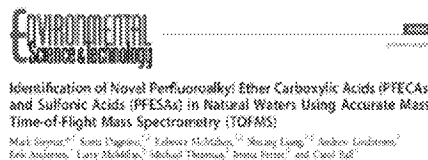
Why NERL/EMMD?

- Historical knowledge / expertise / research on Cape Fear River

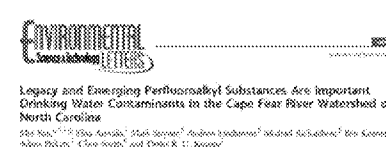
2007



2015



2016



- Unique non-targeted analytical laboratory capability
 - “If it can’t be measured, it is as though it doesn’t exist.”
 - We have no preconceived notions or lists
 - 1,000s – 10,000s of chemicals
 - Being applied to dust, soil, food, air, water, products, plants, animals, and humans

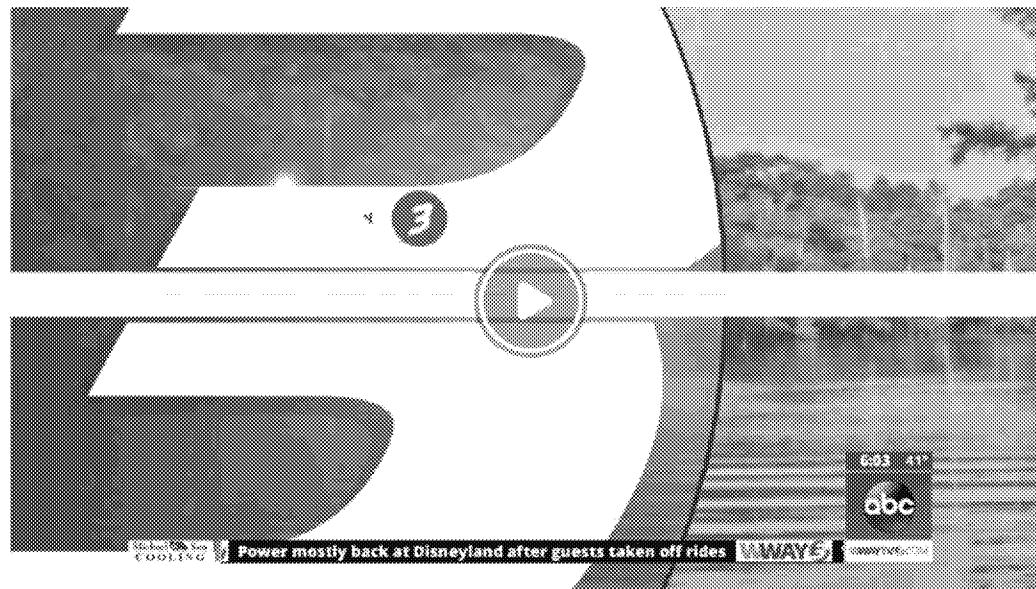


4/4/2018

GenX dominates the news in 2017

GENX DOMINATES THE NEWS IN 2017

By **Reed John** - December 27, 2017 10:50 PM



WILMINGTON, NC (WWAY) — On June 7th, the Starnews broke the story about GenX in the Cape Fear River. As the region learned about this compound from the Chemours chemical plant near Fayetteville in the drinking water supply, citizens wanted answers.

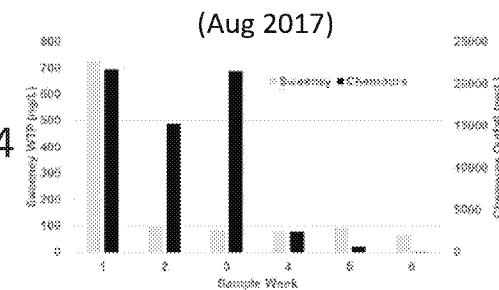
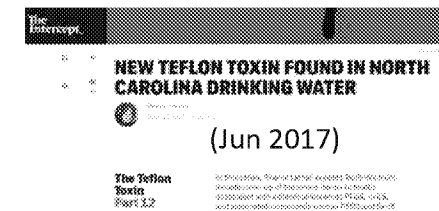
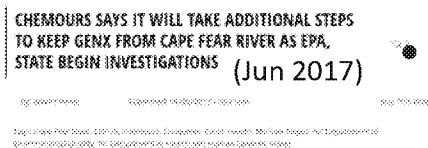
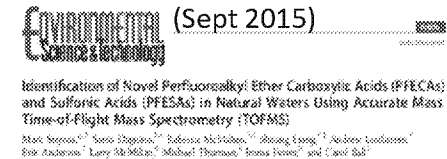
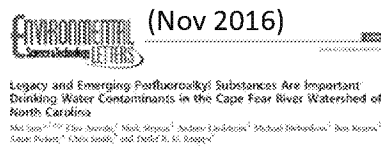
<https://www.wwaytv3.com/2017/12/27/genx-dominates-the-news-in-2017/>

1/4

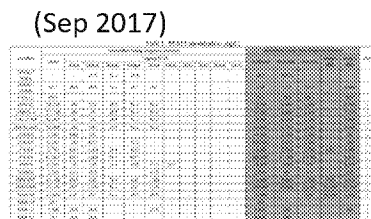
<https://www.wwaytv3.com/2017/12/27/genx-dominates-the-news-in-2017/>

A Case-in-Point for Research that is Relevant, Actionable, and Impactful

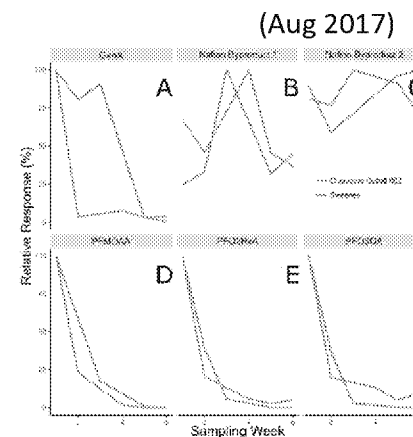
- Non-targeted analysis reveals previously unknown PFAS drinking water contamination
- GenX quantified in drinking water
- Local news media picks up research reports
- Chemours mitigates GenX discharge to Cape Fear River
- NC DEQ, EPA (including Region 4 and ORD) partner to monitor mitigation effectiveness



A Case-in-Point for Research that is Relevant, Actionable, and Impactful (Cont.)



- Non-targeted analysis shows PFESA byproduct discharge unaffected by GenX mitigation
- ↓
- Chemours' site test wells show high-level GenX & PFESA byproduct contamination leading to concern over near-by drinking wells
- ↓
- NC DEQ & Chemours test near-by residents' well/drinking water for GenX & PFESA



(in process)

NC DEQ Takes Action

FILED

STATE OF NORTH CAROLINA 2017 SEP -8 IN THE GENERAL COURT OF JUSTICE
COUNTY OF BLADEN BLADEN COUNTY, N.C. SUPERIOR COURT DIVISION
17 CV8 580

STATE OF NORTH CAROLINA, *ex rel.*,
MICHAEL S. REGAN, SECRETARY,
NORTH CAROLINA DEPARTMENT OF
ENVIRONMENTAL QUALITY,
Plaintiff,
v.
THE CHEMOURS COMPANY FC, LLC,
Defendant.

PARTIAL CONSENT ORDER

NOW THEREFORE, upon the consent of the parties, it is hereby ORDERED,
ADJUDGED AND DECREED that:

1. Chemours shall continue the measures it has implemented to prevent the discharge of process wastewater containing GenX (HFPO dimer acid) into waters of the State.
2. Chemours shall immediately prevent the discharge of PFESA compounds referenced in Paragraph 57 of the Complaint in this matter from what Chemours has represented to be the single source of significance in terms of discernible levels of these compounds, and shall continue to prevent the discharge of the same from this source until such time as an NPDES permit with appropriate permit conditions authorizing any such discharge is issued;

State directs Chemours to provide residents with bottled water after GenX found in preliminary well tests

RALEIGH – State officials have directed Chemours to provide bottled water to 11 homeowners near the company's Fayetteville Works facility after the company's preliminary test results showed GenX above state health goals in residential drinking wells.

The state Department of Environmental Quality and Chemours started testing residential wells near the facility after GenX was detected in 13 industrial, non-drinking water wells on the facility's property. Chemours is testing the private wells for GenX. DEQ is testing private wells near the facility also, but in addition to testing for GenX, the state agency is also testing for two other fluorinated compounds, PFOA and PFOS. The state agency is testing for the three fluorinated compounds because they all have established health goals. The state expects its test results in the coming weeks.

To date, Chemours has received preliminary test results for 32 residential wells for people living near the facility. GenX was not detected in 13 residential wells. GenX concentrations were found below the state's provisional health goal of 140 parts per trillion for eight other residential wells. The 11 homeowners with GenX levels above the state's provisional public health goal were supplied with bottled water and health information about GenX. Most of the 11 wells with elevated GenX levels are north of the facility.

The company's test results have not been validated. Out of an abundance of caution, the state directed the company to supply bottled water to residents after receiving word Friday of the first batch of preliminary test results, and then again on Tuesday when Chemours notified the state of another batch of preliminary results.

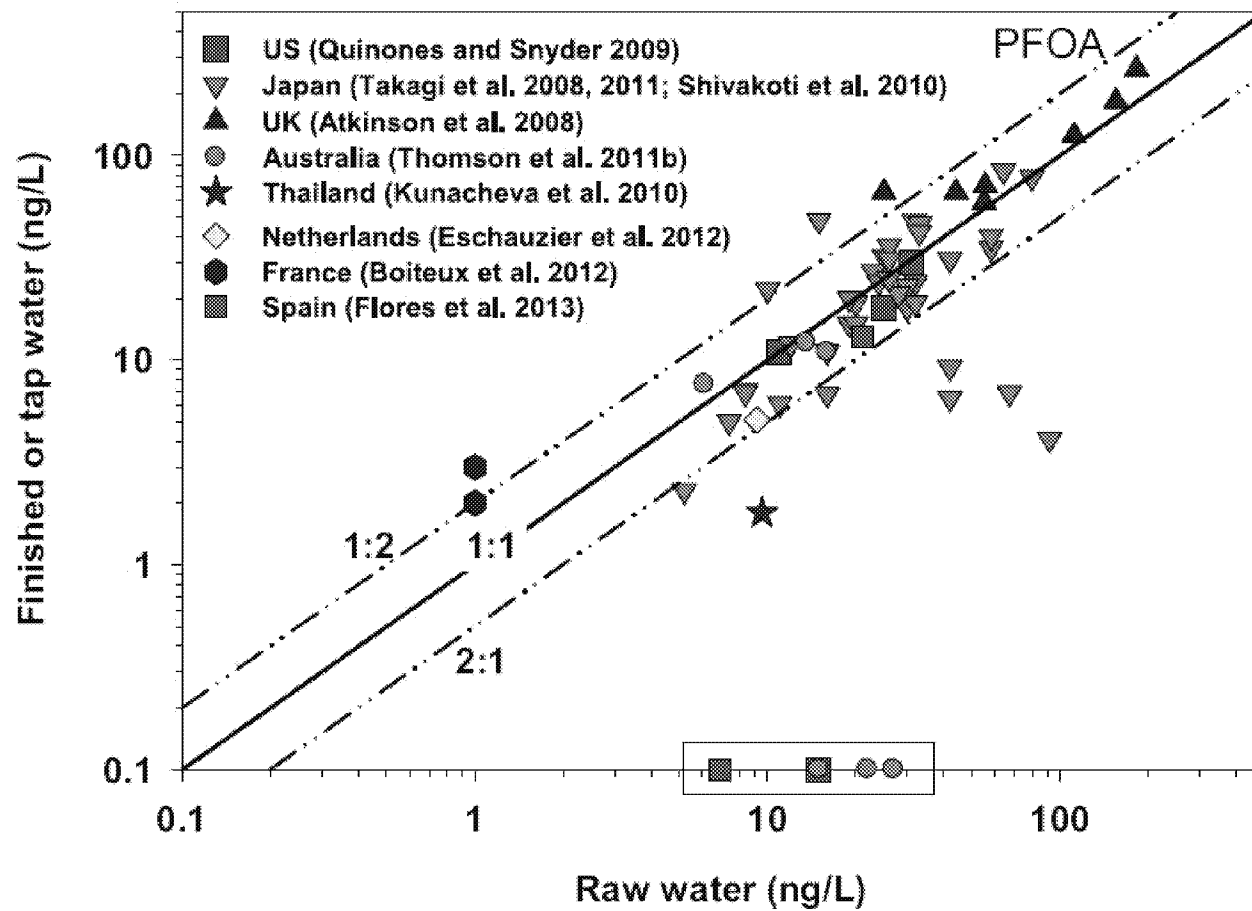
"We want to make sure people with elevated concentrations of GenX in their wells have an immediate alternative water source," said Michael Regan, secretary of the N.C. Department of Environmental Quality. "Making sure people have clean drinking water is our top priority."

This week, DEQ has continued collecting water samples for residential wells nearest the facility. As of Wednesday, DEQ had collected water samples for 31 residential wells in Bladen and Cumberland counties. The state will send samples to Gel Laboratories in Charleston, S.C. for analysis and use the results of testing to determine if people need alternative sources of water and if GenX or the two other fluorinated compounds produced at the facility have moved into the surrounding community. If tests reveal levels of any of the fluorinated compounds above established health goals, the state will direct Chemours to provide affected homes with alternative water and health information on the compounds.

It's important to understand that the state's provisional health goal for GenX represents the concentration of GenX at which no adverse, non-cancer health effects would be anticipated in the most sensitive populations over an entire lifetime of exposure.

Health-related information on GenX, PFOA and PFOS has been posted to DEQ's website at: <https://deq.nc.gov/news/hot-topics/genx-investigation/health-related-resources-about-genx-pfoa-and-pfos>. Residents with questions about the health effects related to GenX, PFOA or PFOS can contact the N.C. Department of Health and Human Services at 919-707-5900.

PFAS Generally Not Removed During Conventional Drinking Water Treatment

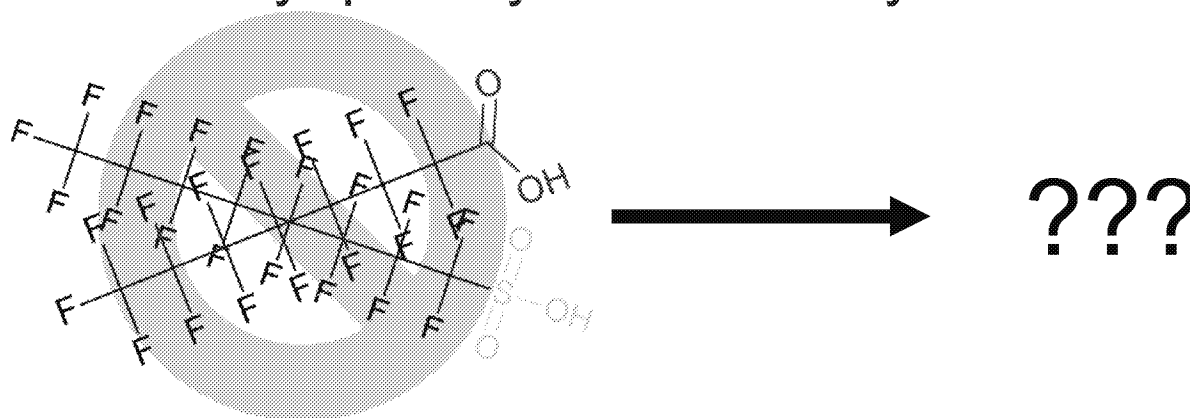


Similar for PFOS, PFHxA and PFHxS

Rahman et al., (2014) *Water Research*, 50:318-340

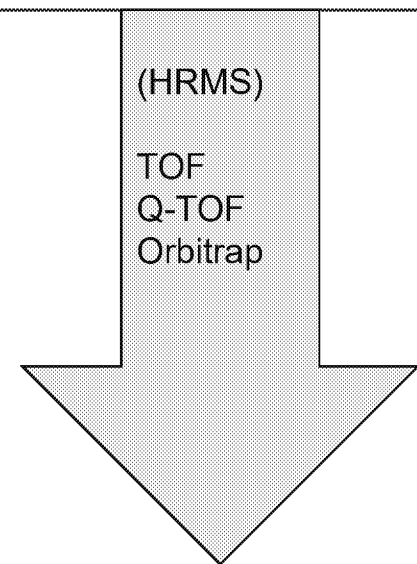
OTHER PFASs: The Era of HRMS & Non-Targeted Analysis

- How do we find compounds without knowing what they are?
- How do we prioritize unknowns for further analysis?
- How do we identify/quantify without analytical standards?

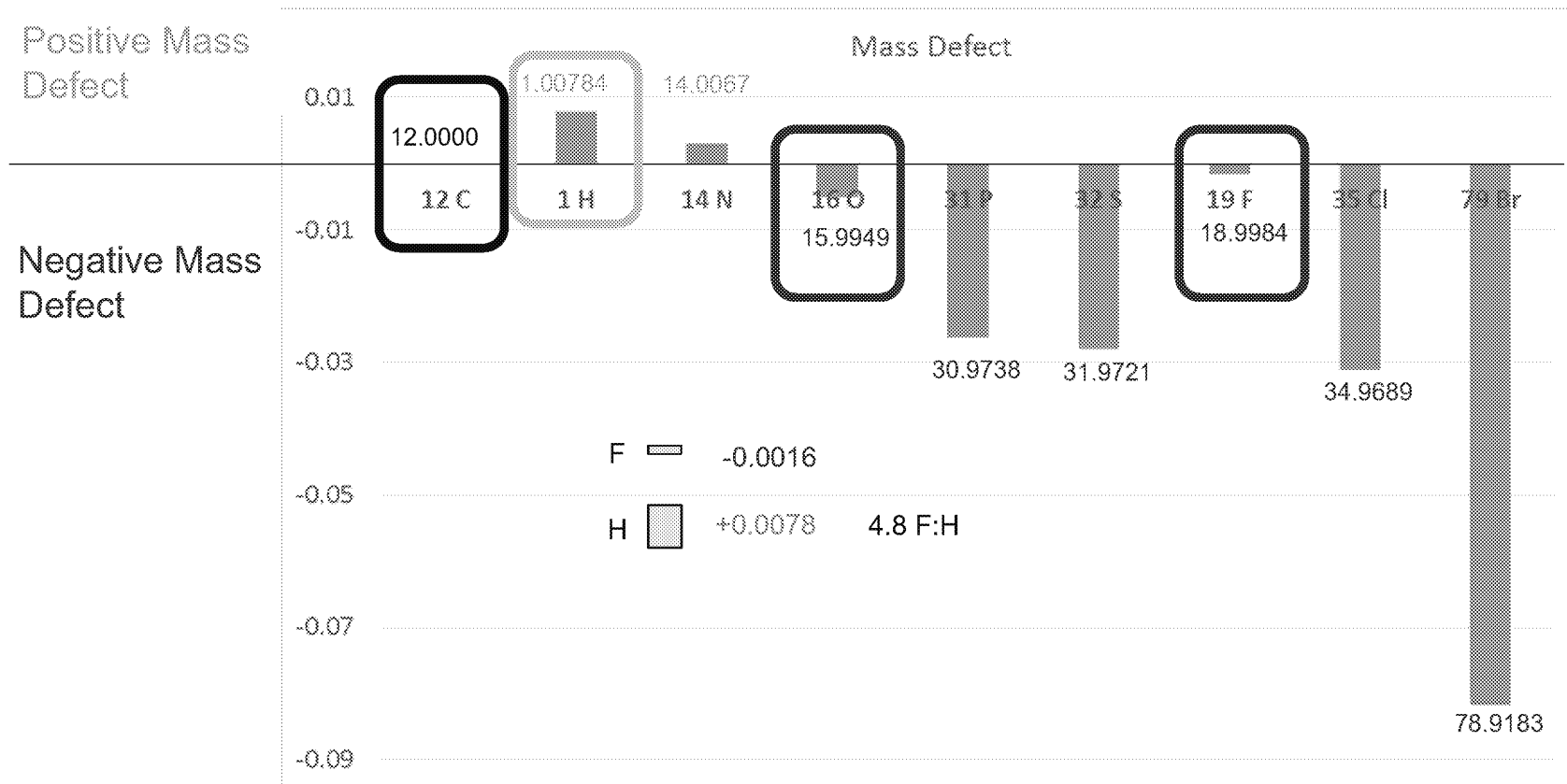


What is Non-Targeted Analysis

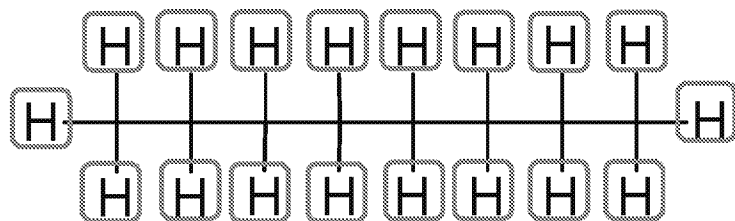
- Targeted Analysis
 - How much PFOA is in my sample?
- Suspect Screening
 - Which chemicals in this database are in my sample?
- Non-Targeted Screening
 - What are the chemicals in my sample?



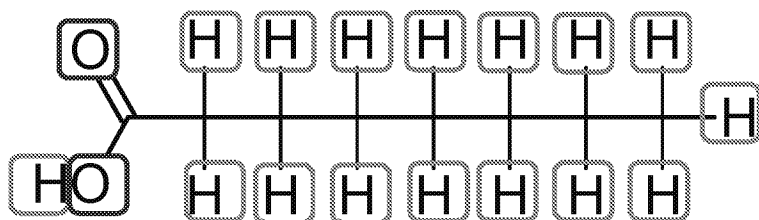
Isotope Signatures: Negative Mass Defect



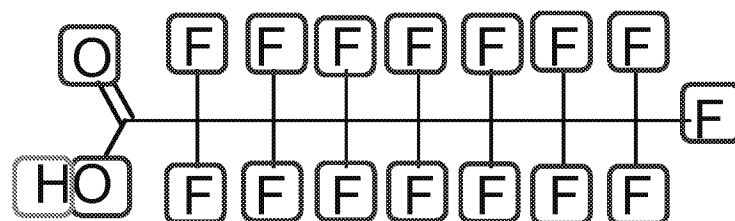
Example of Mass Defect



Octane
MI mass 114.1409



Octanoic Acid
MI mass 144.1150

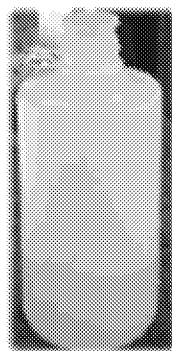


Perfluorooctanoic Acid
MI mass 413.9737

Negative Mass Defect

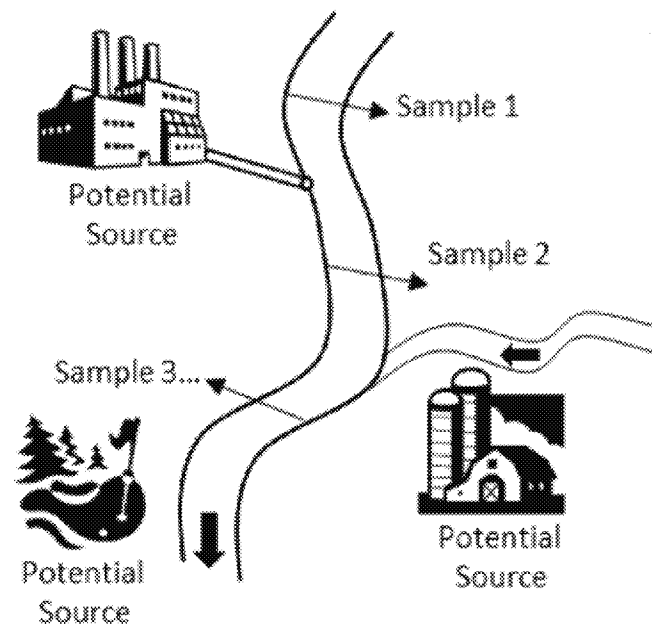
Data Generation: Source Determination by NTA

Surface Water
Ground Water
WWTP Effluent
Drinking Water



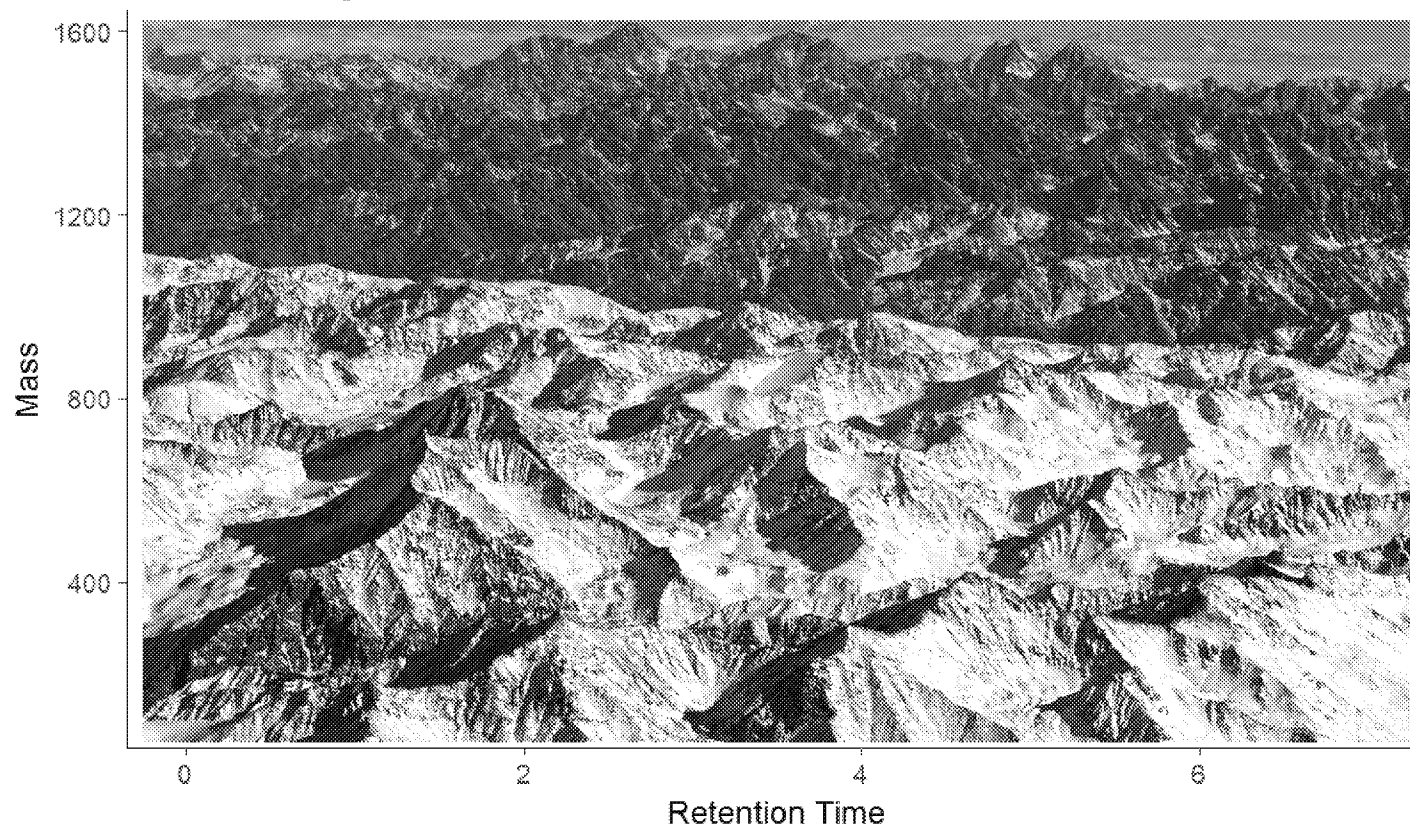
HDPE Bottles

Sampling from geographically or temporally displaced locations allows triangulation of sourcing



Strynar et al. *Environ. Sci. Technol.*, **2015**, 49 (19), pp 11622–11630

Typical HRMS Mass + RT Pairs



Past Work: PFAS in NC Water



Nakayama et al. 2007 *ES&T* 41:5271-5276

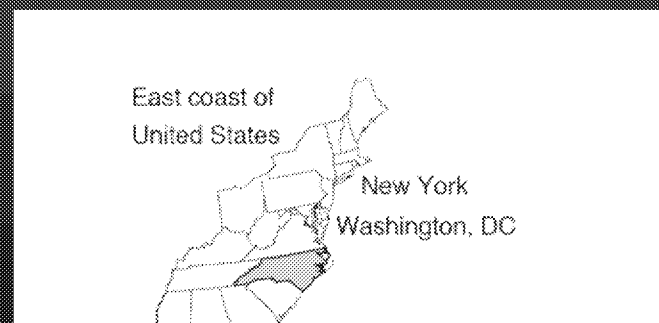
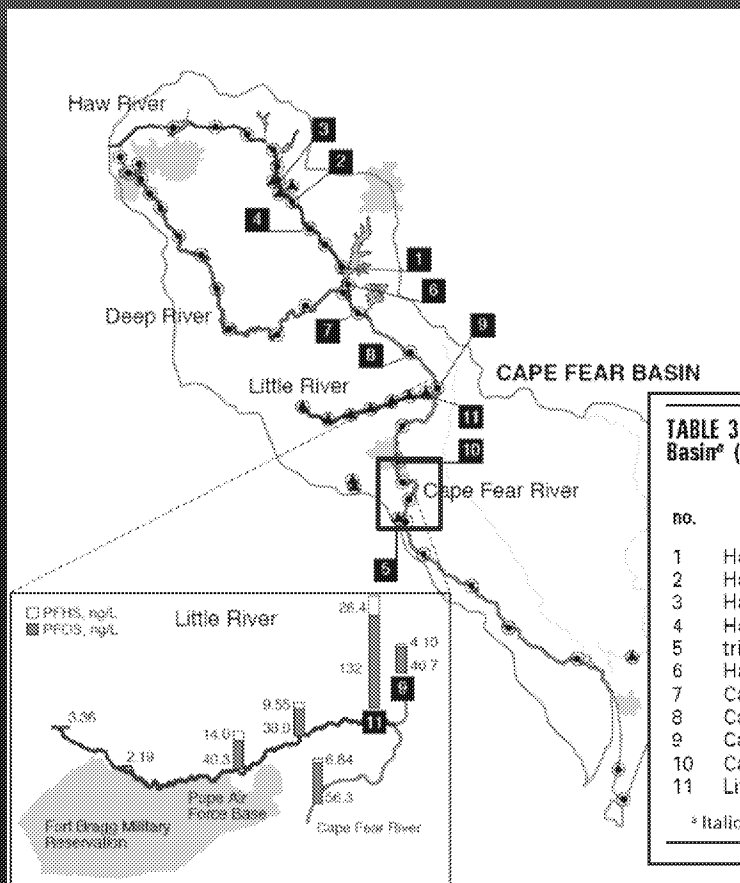


TABLE 3. Measured Concentrations at the Eleven Sites with the Highest Total Concentrations of PFCs in the Cape Fear River Basin^a (See Figure 1 for locations)

no.	river	C12 (ng/L)	C11 (ng/L)	C10 (ng/L)	C9 (ng/L)	C8 (ng/L)	C7 (ng/L)	C6 (ng/L)	PFOS (ng/L)	PFHS (ng/L)	PFBS (ng/L)	total (ng/L)
1	Haw River	<i>4.46</i>	<i>52.1</i>	<i>120</i>	<i>194</i>	<i>287</i>	118	21.7	127	8.43	<i>9.41</i>	942
2	Haw River	3.20	28.7	112	157	200	66.8	14.5	33.4	7.87	2.61	626
3	Haw River	3.29	27.6	109	157	191	59.2	13.7	36.4	9.49	3.04	609
4	Haw River	1.98	20.0	89.2	151	201	58.2	13.2	31.5	7.49	2.88	574
5	tributary to Cape Fear	2.26	15.0	19.6	71.2	58.6	329	23.0	30.0	3.36	ND	531
6	Haw River	1.18	8.87	31.0	72.1	152	58.3	13.5	31.2	7.70	ND	376
7	Cape Fear River	< LOQ	3.34	13.2	34.8	70.3	24.0	7.84	66.7	5.59	ND	227
8	Cape Fear River	1.14	6.39	17.2	35.7	71.5	26.9	9.35	50.4	4.82	ND	223
9	Cape Fear River	1.23	6.75	17.1	38.0	72.7	23.7	7.05	40.7	4.10	ND	211
10	Cape Fear River	< LOQ	7.55	19.3	31.2	46.8	13.9	4.62	56.3	6.84	2.12	189
11	Little River	< LOQ	< LOQ	2.17	2.24	12.6	3.38	3.23	132	26.4	3.20	185

^a Italicized values show maximal concentrations of each compound.

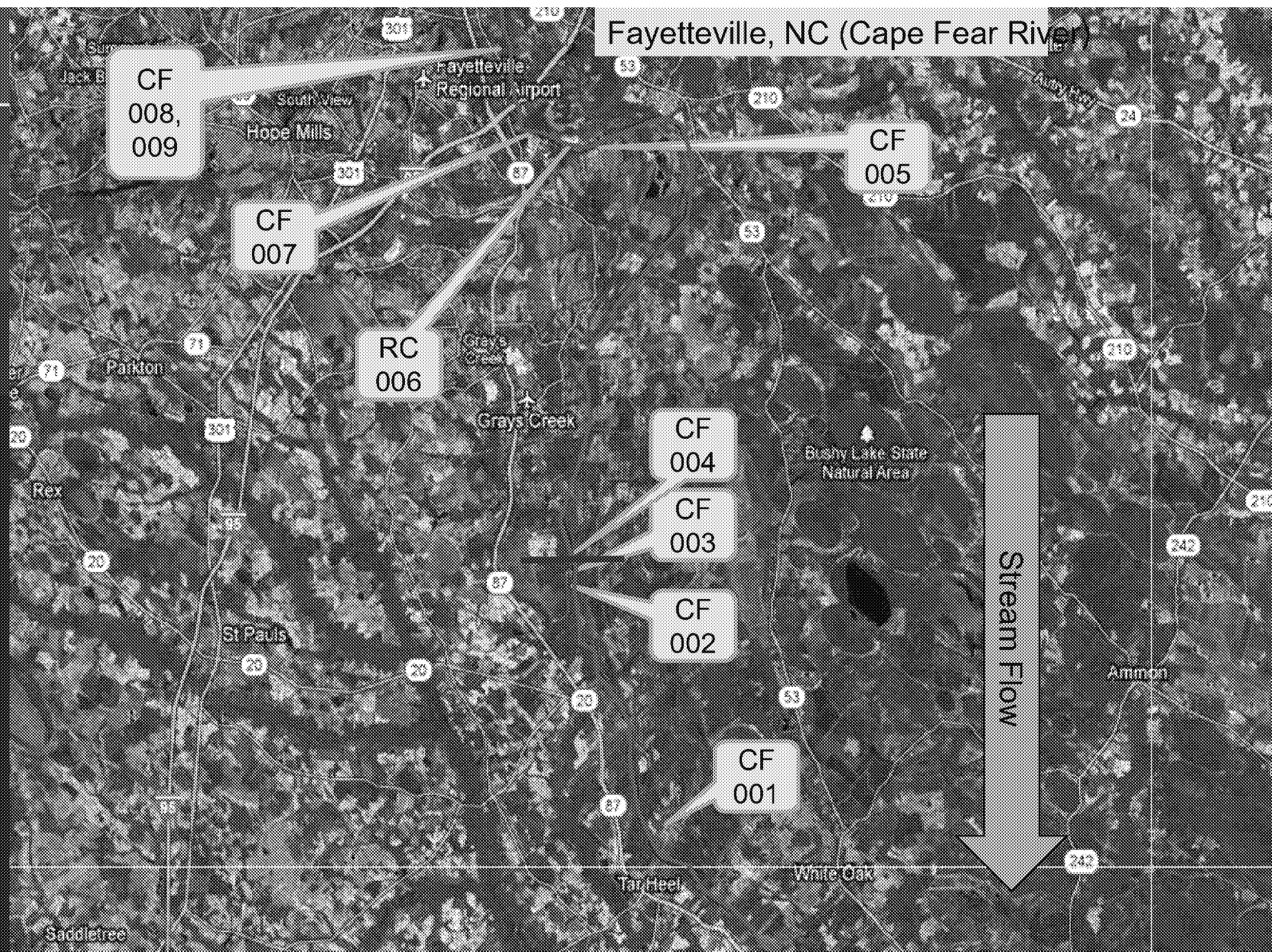
U.S. Environmental Protection Agency

First Sampling
2011-2012

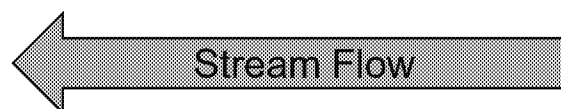
Presented at
SETAC 2012

Follow-up sampling
2013-2013

Presented at
SETAC 2014



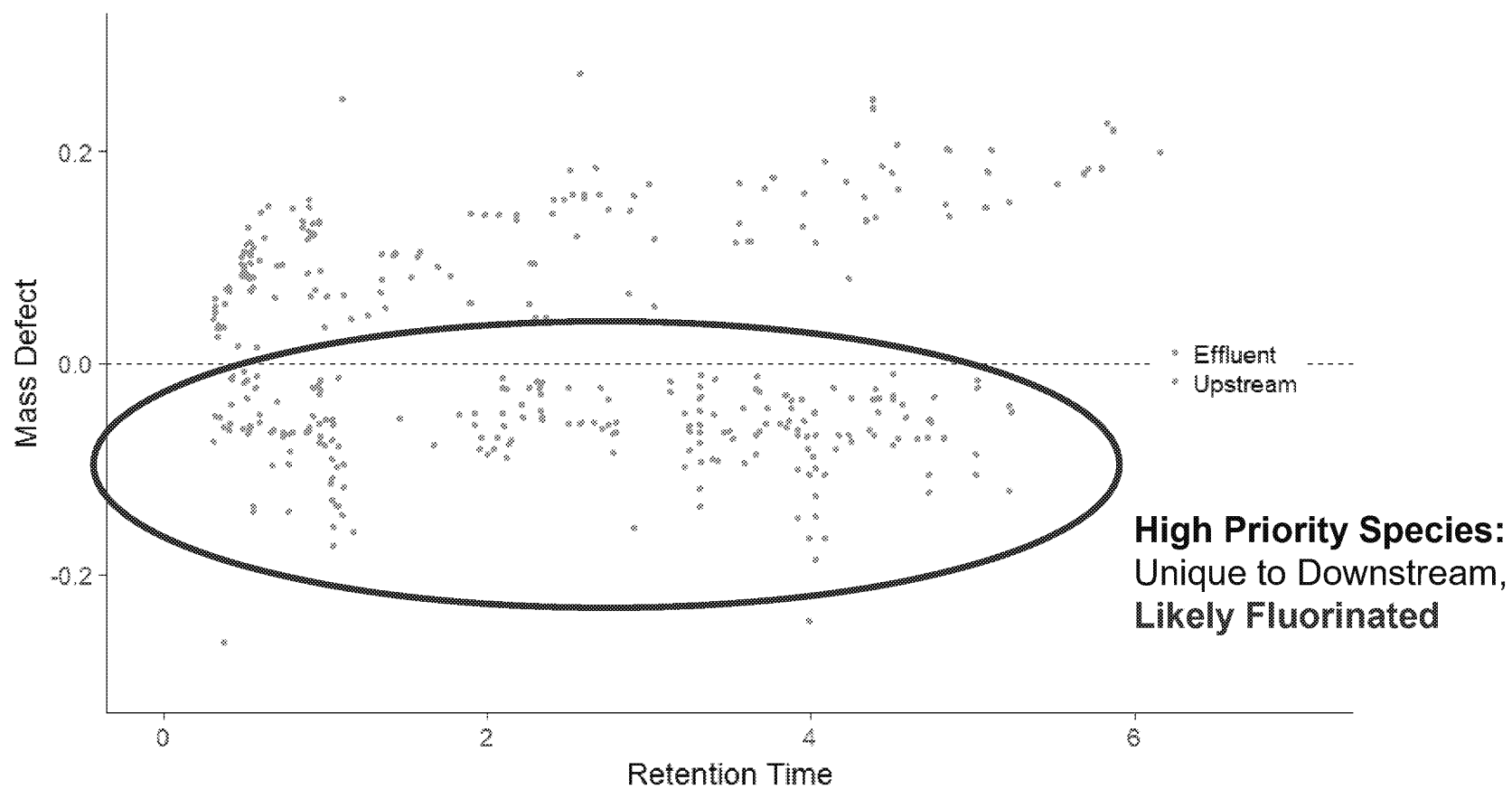
Legacy PFAS found in Cape Fear Water circa 2012



Analyte	001	002	003	004	005	006	007	008	008	009
C4	23	502	3761	6	4	0	8	7	5	3
C5	441	5607	43590*	17	9	1	32	46	12	9
PFBS	4	5	3	4	5	2	9	5	6	4
C6	17	90	434	18	12	2	27	16	18	14
C7	37	599	3873	14	17	0	11	20	21	9
PFHS	7	12	10	9	7	4	9	10	9	22
C8	32	39	71	33	25	2	38	36	41	18
C9	13	34	127	7	11	1	6	8	11	5
PFOS	19	27	26	17	23	0	0	16	18	14
C10	10	17	12	11	0	3	3	8	10	5

items in red exceed the standard curve high end of 500 ng/L; 10x diluted and re-analyzed; * still exceed curve and are estimated

Mass Defect of Outfall and Upstream Features



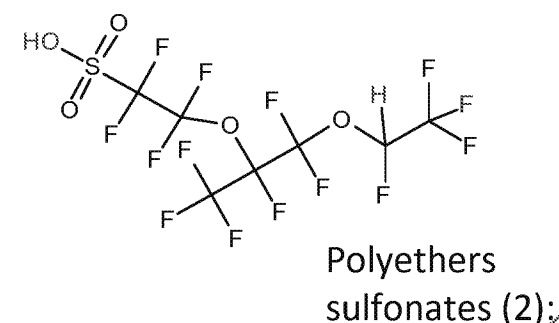
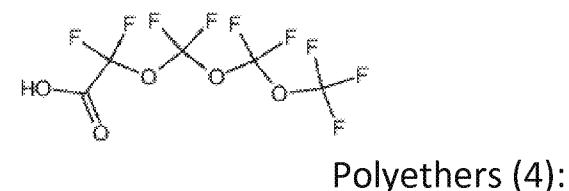
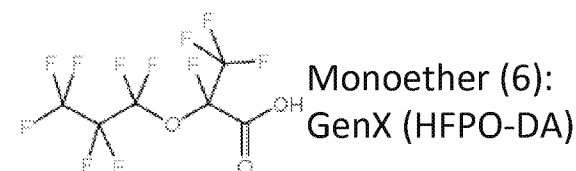
Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)

Mark Strynar,^{*,†} Sonia Dagnino,^{‡,§} Rebecca McMahan,^{‡,§} Shuang Liang,^{‡,§} Andrew Lindstrom,[†] Erik Andersen,[†] Larry McMillan,[§] Michael Thurman,^{||} Imma Ferrer,^{||} and Carol Ball¹

Table 1. Accurate Mass of Polyfluorinated Compounds and In-Source Artifacts Found in Extracted Water Samples

number	formula	CAS no.	name	[M] ⁺	[M - H] ⁺ m/z	[2M - 2H + Na] ⁺ m/z	[2M - H] ⁺ m/z
Monoether PFECAs							
1	C ₃ HF ₉ O ₃			179.9846	178.9773	380.9438	358.9619
2	C ₆ HF ₉ O ₃			229.9813	228.9740	480.9372	458.9553
3	C ₉ HF ₉ O ₃	863090-89-5		279.9782	278.9709	580.9310	558.9491
4	C ₆ HF ₁₁ O ₃	13252-13-6	undecafluoro-2-methyl-3-oxahexanoic acid	329.9750	328.9677	680.9247	658.9427
5	C ₇ HF ₁₃ O ₃			379.9718	378.9645	780.9182	758.9363
6	C ₈ HF ₁₅ O ₃			429.9686	428.9613	880.9118	858.9299
Polyether PFECAs							
7	C ₇ HF ₁₃ O ₇	39492-91-6	perfluoro-3,5,7,9,11-pentaoxadodecanoic acid	443.9515	442.9442	908.8776	886.8957
8	C ₈ HF ₁₁ O ₆	39492-90-5	perfluoro-3,5,7,9-butoxadecanoic acid	377.9598	376.9525	776.8942	754.9123
9	C ₉ HF ₉ O ₅	39492-89-2	perfluoro-3,5,7-propaoxaoctanoic acid	311.9681	310.9608	644.9108	622.9289
10	C ₄ HF ₇ O ₄	39492-88-1	perfluoro-3,5-dioxahexanoic acid	245.9764	244.9691	512.9274	490.9455
PFESAs							
11	C ₇ HF ₁₃ O ₃ S	66796-30-3 ^b		443.9337	442.9264		
12	C ₇ H ₂ F ₁₆ O ₃ S			463.9399	462.9326		

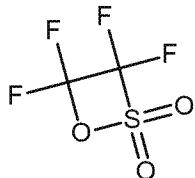
Example Structures



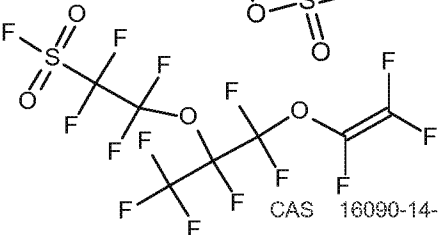
Chemours Site TSCA Inventory

Sulfonates

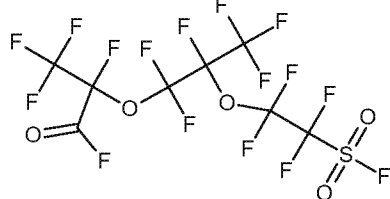
CAS 697-18-7



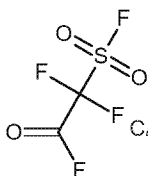
CAS 16090-14-5



CAS 4089-58-1

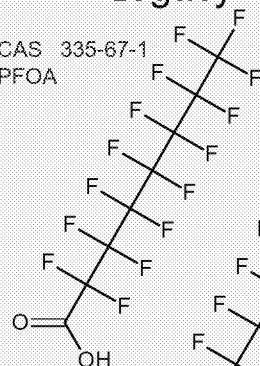


CAS 677-67-8

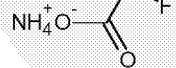
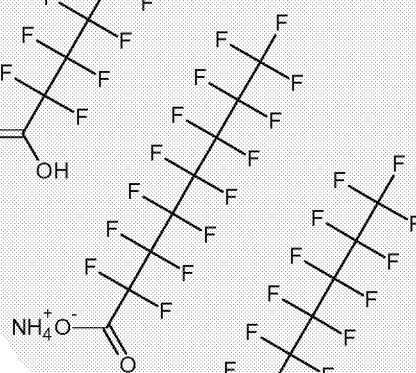


Legacy

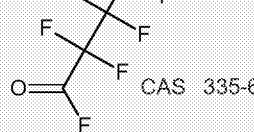
CAS 335-67-1
PFOA



CAS 3825-26-1
APFO

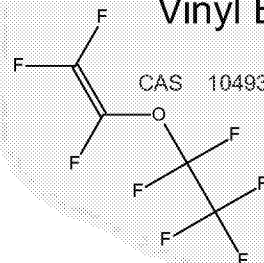


CAS 335-66-0

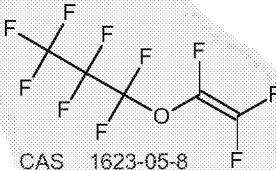
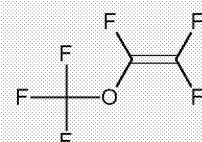


Vinyl Ethers

CAS 10493-43-3



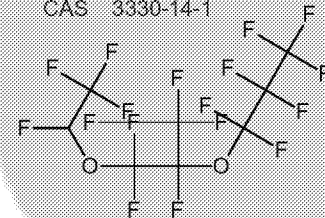
CAS 1187-93-5



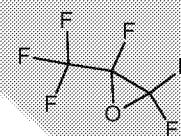
CAS 1623-05-8

Other

CAS 3330-14-1

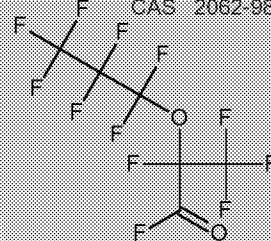


CAS 428-59-1

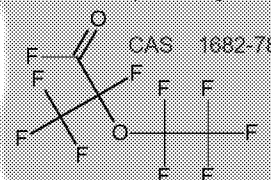


Acid Fluorides

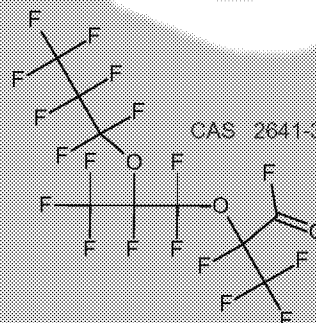
CAS 2062-98-8



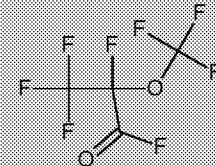
CAS 1682-78-6



CAS 2641-34-1



CAS 2927-83-5



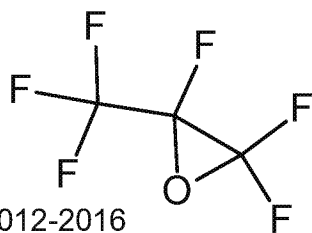
DUPONT FAYETTEVILLE PLANT
22828 NC HIGHWAY 87 WEST
FAYETTEVILLE, NC 28306-7332

http://iaspub.epa.gov/enviro/tsca.get_chem_info?v_registry_id=110000559609

Hexafluoropropylene Oxide (HFPO) Based Chemistry

HFPO

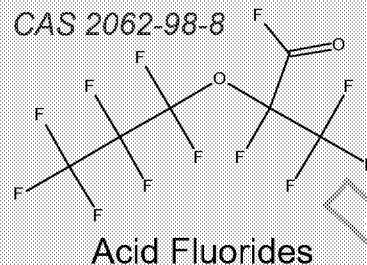
CAS 428-59-1



2012-2016
Estimated emission
36k-77k lb/yr

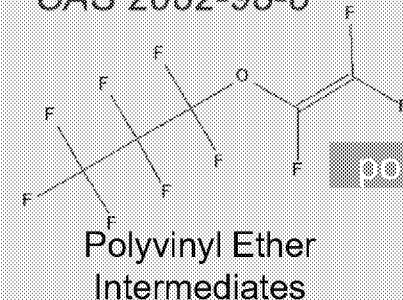
Dimerized to
HFPO-DAF

HFPO-DAF
CAS 2062-98-8

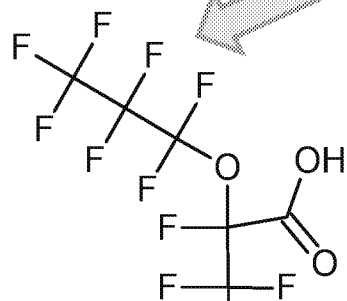


Vinyl Ether Production

CAS 2062-98-8



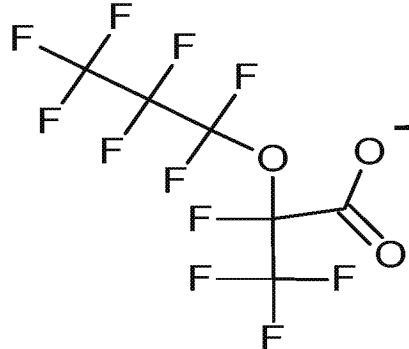
polymers



HFPO-DA
CAS 13252-13-6

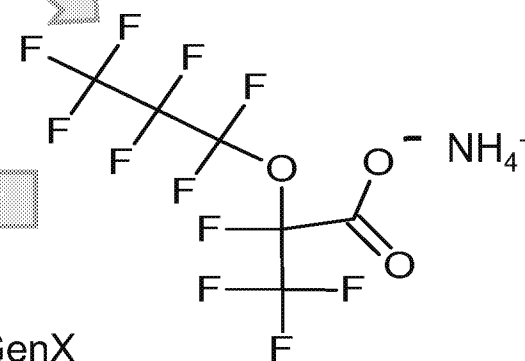
In Water

Common Analyte

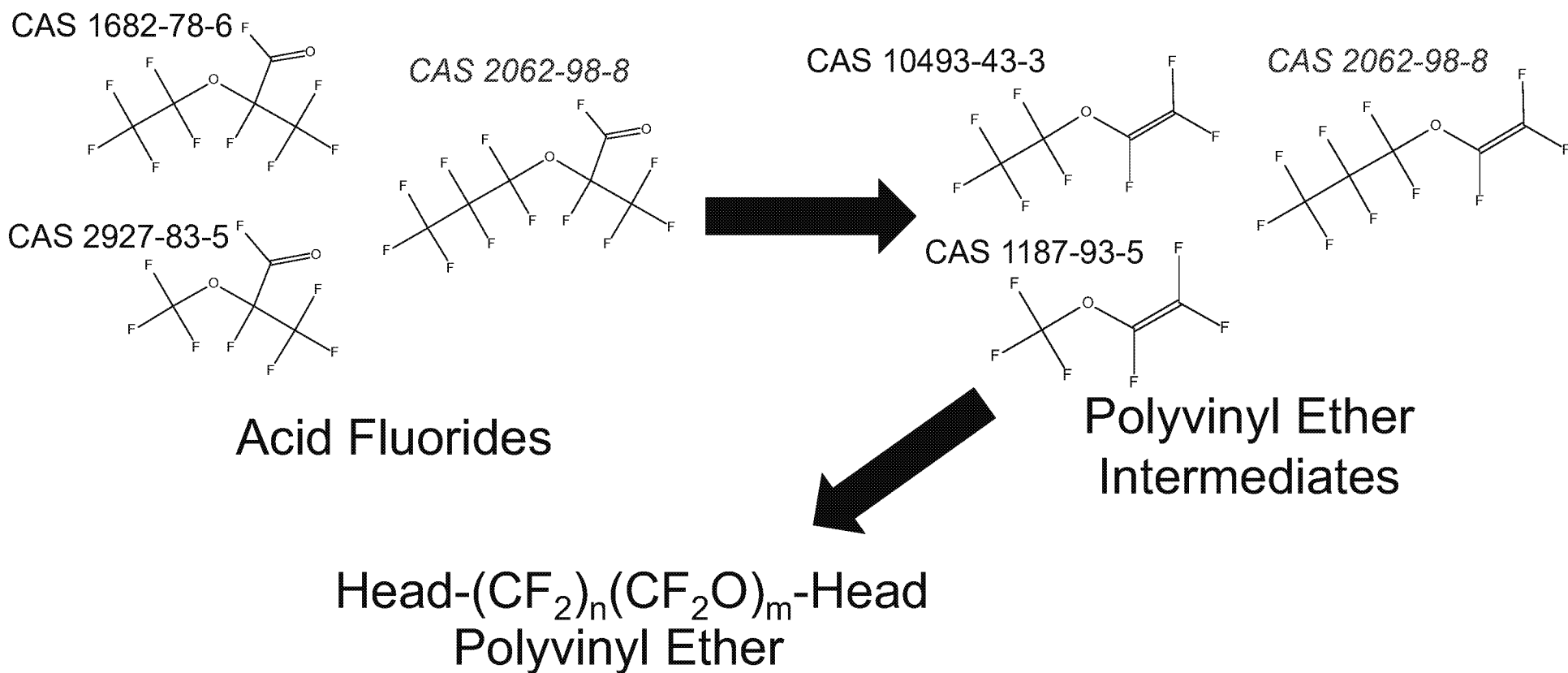


In water

GenX
CAS 62037-80-3

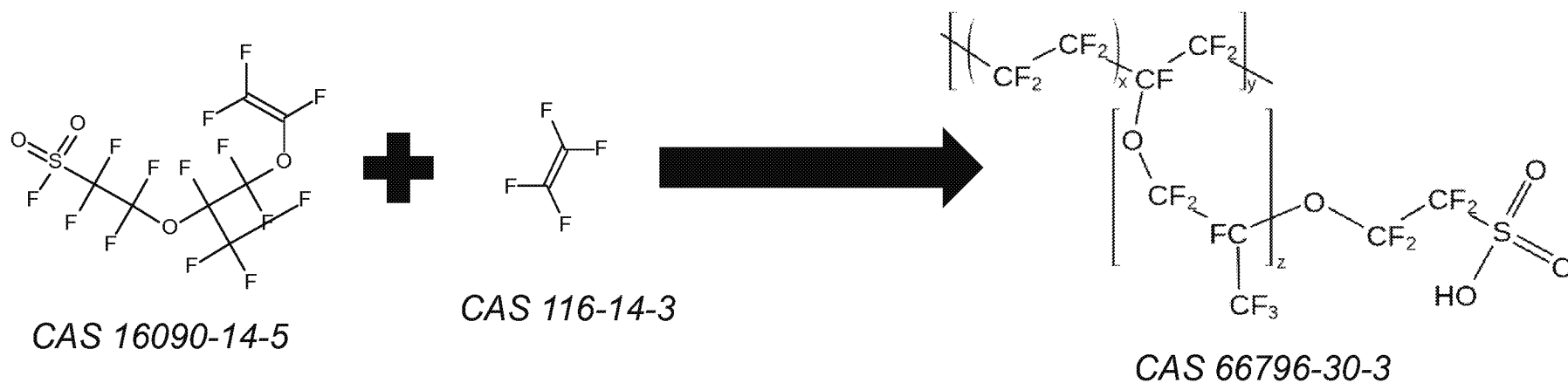


Polyvinyl Ether Production



Nafion Polymer

- Nafion is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer.
- proton conductor for proton exchange membrane (PEM) fuel cells



Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

Mei Sun,^{*,†,‡,§} Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,^{||} Ben Kearns,^{||} Adam Pickett,[⊥] Chris Smith,[#] and Detlef R. U. Knappe[‡]

Toxin taints CFPUA drinking water



MOST POPULAR

1 Carolina Surf condos - in danger of collapse - condemned, evacuated
Jul 9 at 5:58 AM

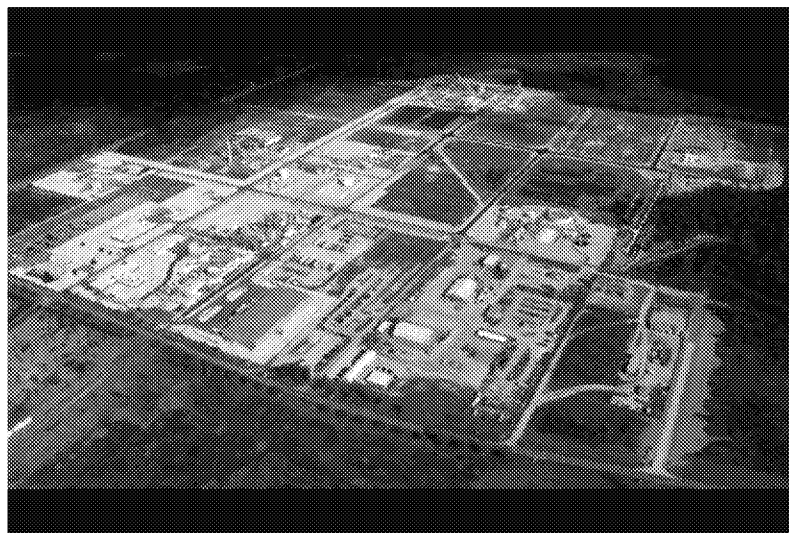
2 Man injured by hook, not hit by shark at Wrightsville Beach
Jun 30 at 1:48 PM

3 Murder suspect had other charges pending
Jul 3 at 5:44 PM

4 Residents not allowed back into Carolina Surf condos
Jul 4 at 7:09 PM

* * * *

OUR PICKS



▲ HIDE CAPTION

A 2000 aerial photo of Fayetteville Works on the Cumberland-Bleaton county line. The site, home to several plants, one of which makes GenX, is about 100 miles upstream from Wilmington. [COURTESY OF THE FAYETTEVILLE OBSERVER]

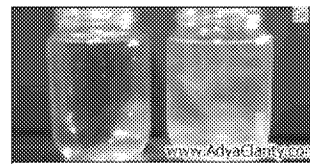
By Vaughn Hagerly StarNews Correspondent

Posted Jun 7, 2017 at 10:33 AM

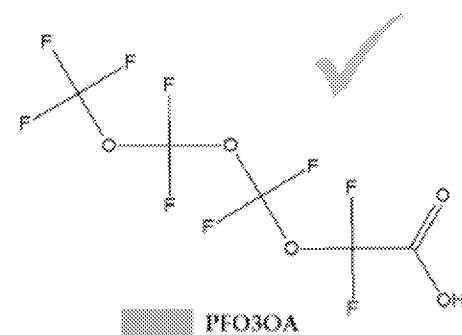
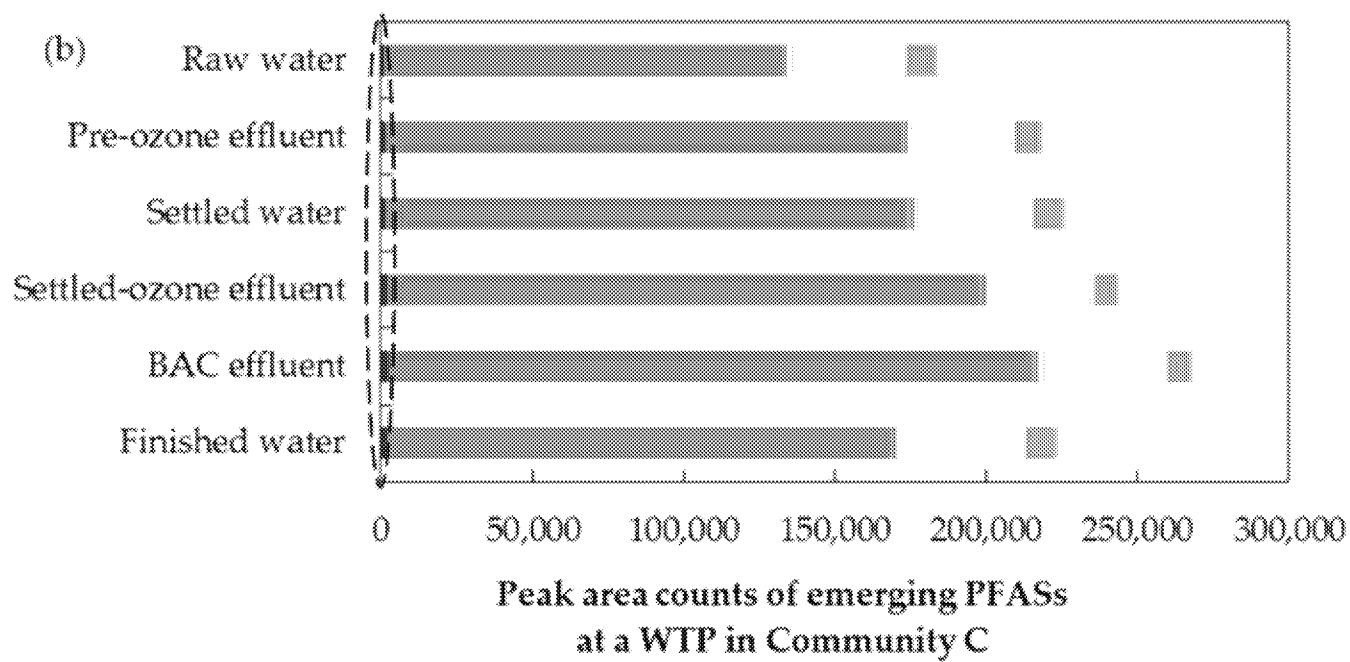
Updated Jun 8, 2017 at 10:36 AM



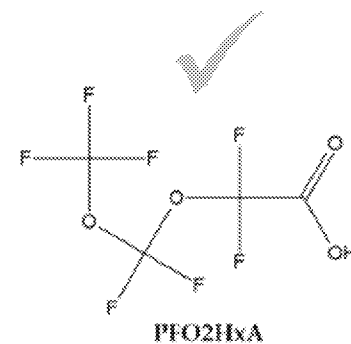
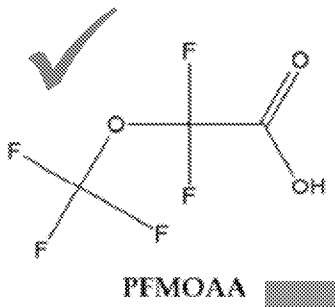
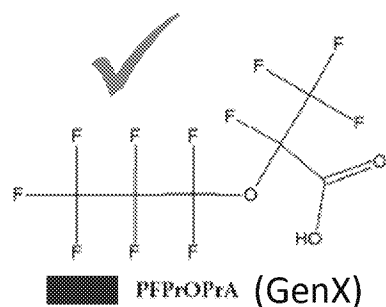
Utility can't filter out chemical produced upriver



Cape Fear River
Fayetteville to Wilmington, NC



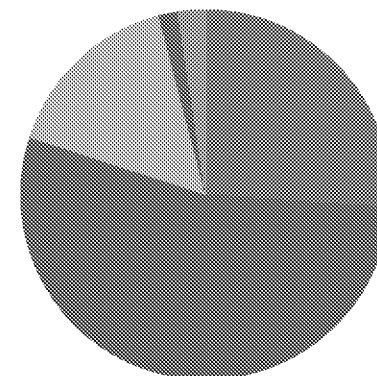
■ PFPPrOPrA ■ PFMObA
 □ PFO2HxA ■ PFO3OA ■ PFMOPrA ■ PFMObA



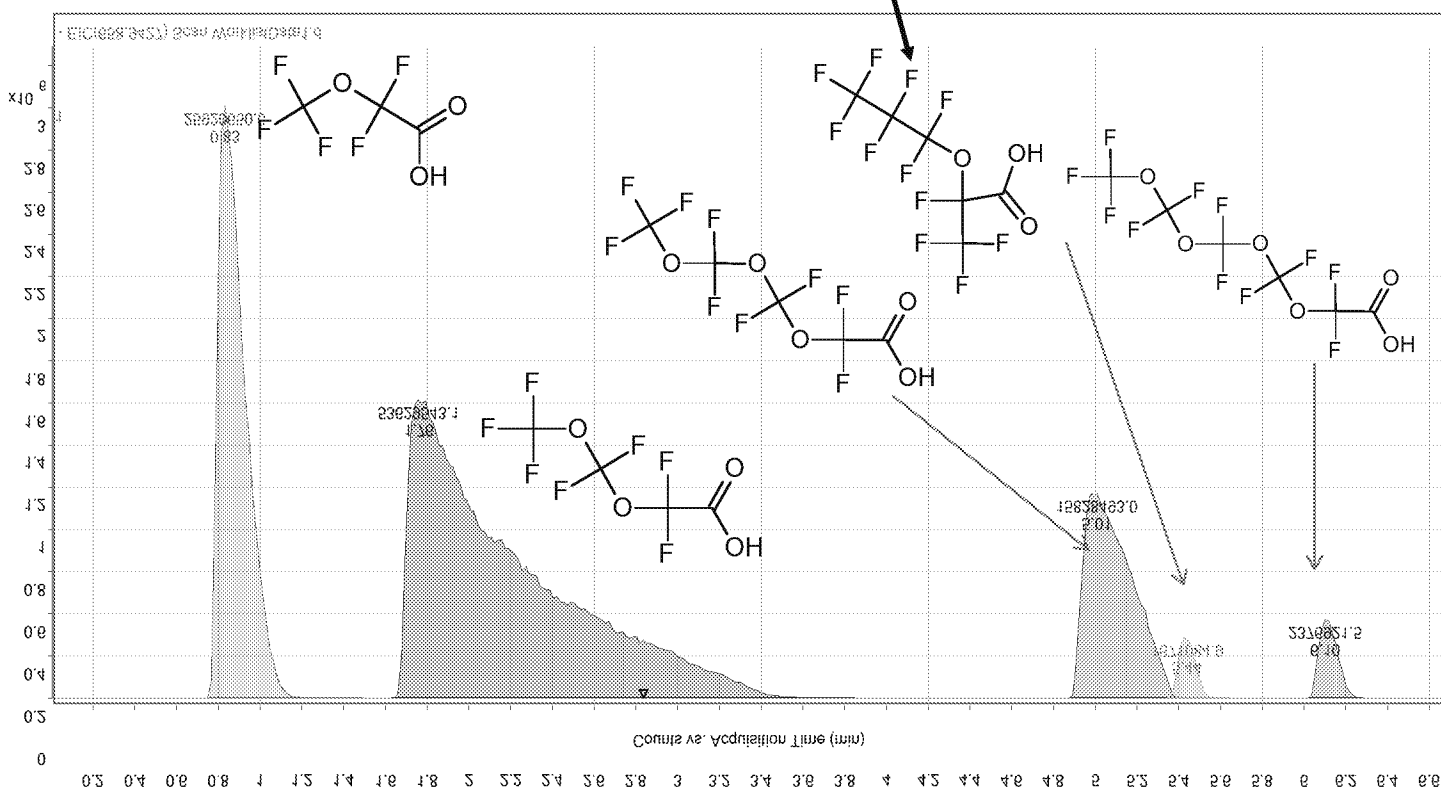
PFECAs in 5-15-17 Cape Fear River Sample

Area

- C3HF5O3
- C4HF7O4
- C5HF9O5
- GenX
- C6HF11O6



GenX



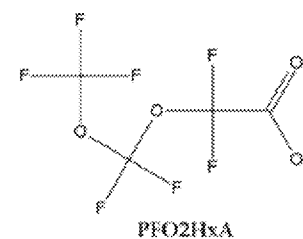
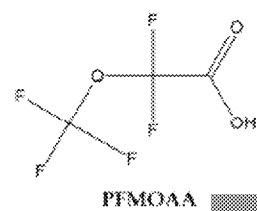
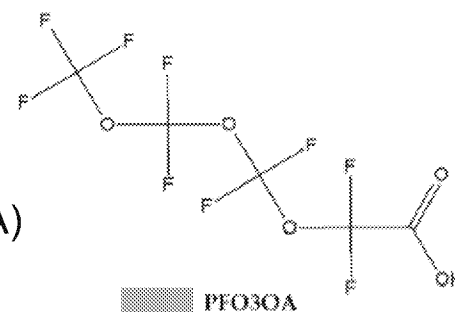
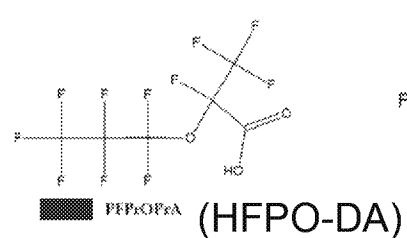
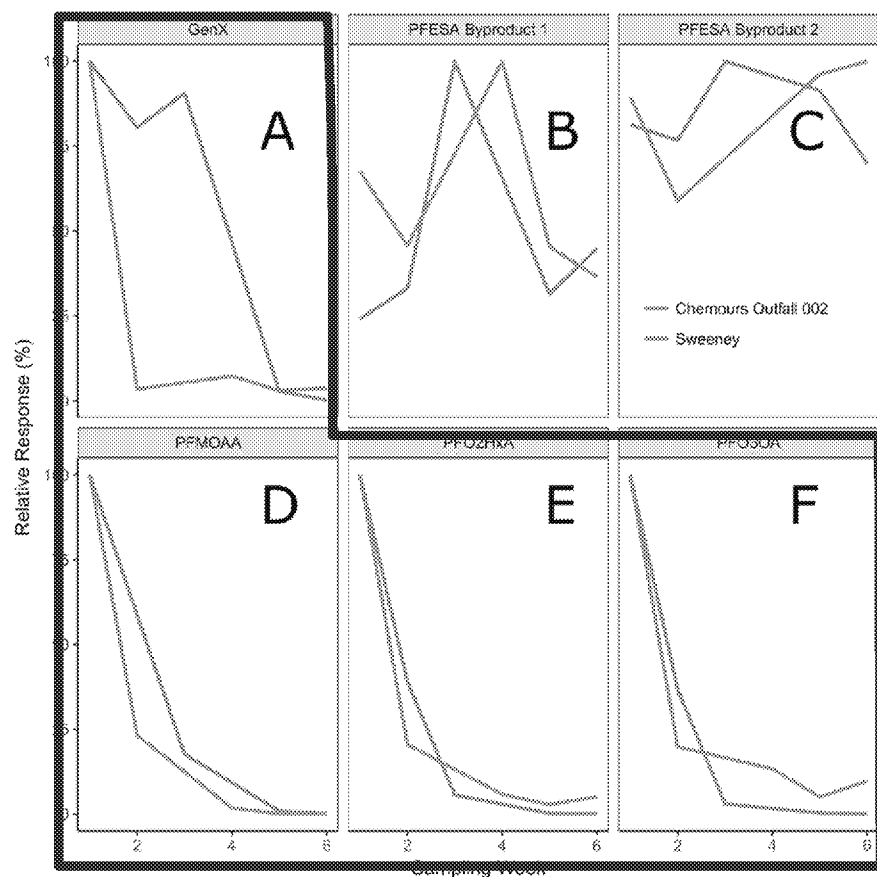


Enter NCDEQ June-October 2017

U.S. Environmental Protection Agency

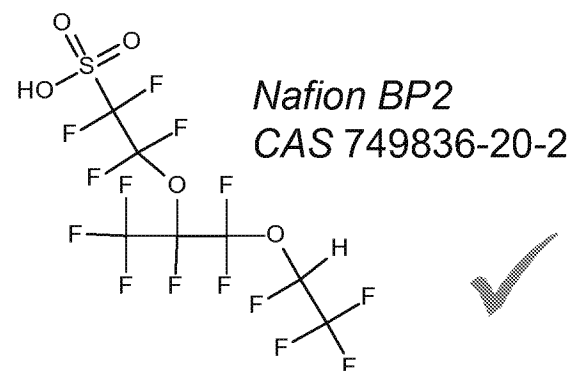
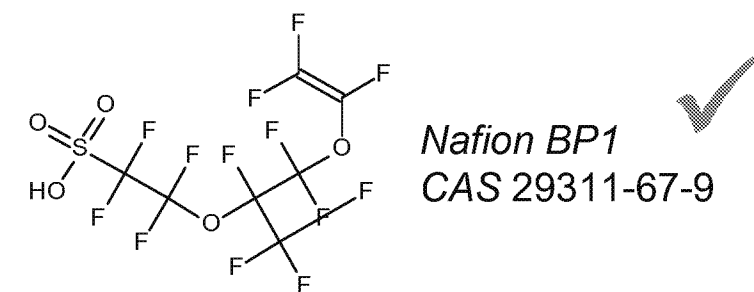
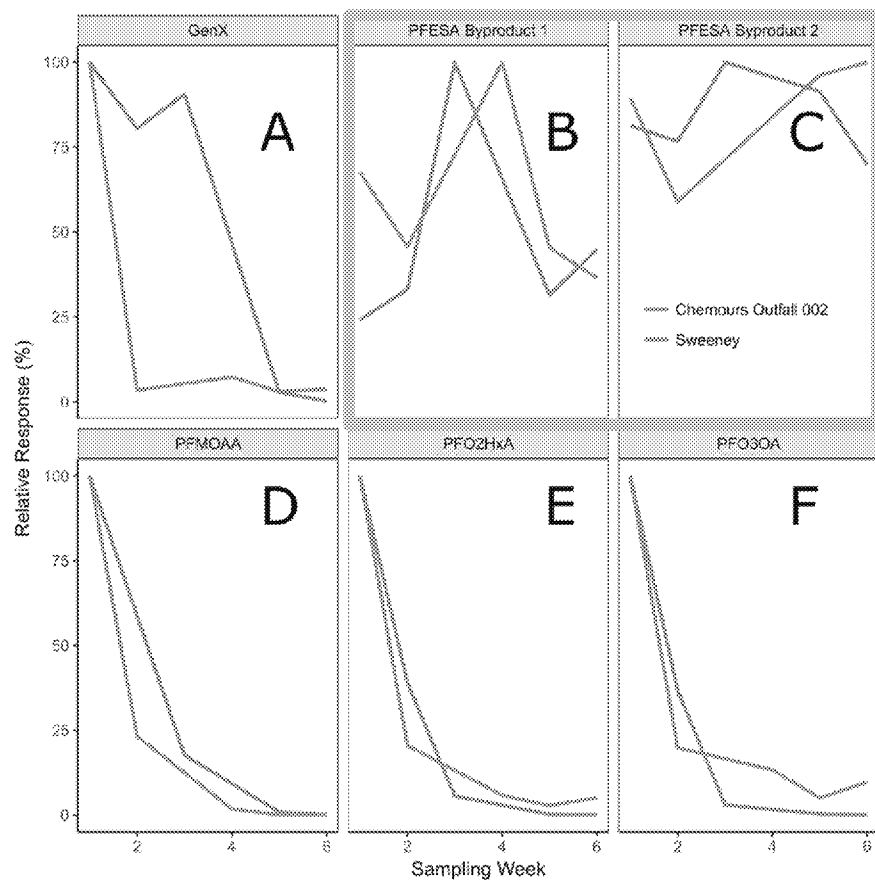
Relative Quantitation Time Trends

6 weeks mid June – early August

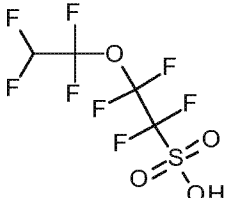


Relative Quantitation Time Trends

6 weeks mid June – early August

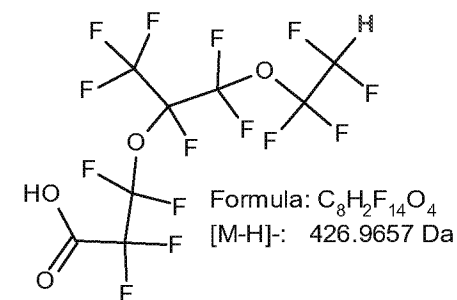
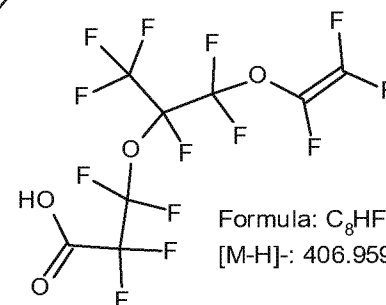


Retrospective Analysis (McCord *in prep*)

Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	✗	✗	✗
	1-26-12	✓	✗	✗	✓	✓	✗	✗	✗
2012	2-1-12	✓	✗	✗	✓	✓	✗	✓	✗
	2-9-12	✓	✓	✓	✓	✓	✓	✗	✗
	5-4-12	✓	✗	✗	✓	✓	✗	✗	✗
	5-4-12	✓	✗	✗	<div><p>Formula: C₄H₂F₈O₄S [M-H]⁻: 296.9473 Da</p></div>	✗	✗	✗	
	2014	11-24-14	✓	✗		✗	✗	✗	✗
2015	5-12-15	✓	✓	✓		✓	✓	✓	
	5-12-15	✓	✓	✓		✓	✓	✓	
2017	8-6-15	✓	✓	✓	✓	✓	✓	✓	
	5-12-17	✓	✗	✓	✓	✓	✓	✓	
	6-20-17	✓	✓	✓	✗	✓	✓	✓	
	6-27-17	✓	✓	✓	✗	✗	✗	✗	
	7-4-17	✓	✓	✓	✓	✓	✗	✗	✗
	7-11-17	✓	✓	✓	✓	✓	✗	✗	✗
	7-18-17	✓	✓	✓	✓	✓	✗	✗	✗
	7-25-17	✓	✓	✓	✓	✓	✗	✗	✗
	8-3-17	✓	✓	✓	✓	✓	✗	✗	✗

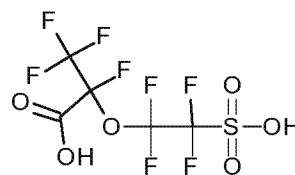
Retrospective Analysis (McCord *in prep*)

Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	x	x	x
	1-26-12	✓	x	x	✓	✓	x	x	x
2012	2-1-12	✓	x	x	✓	✓			
	2-9-12	✓	✓	✓	✓	✓			
	5-4-12	✓	x	x	✓	x			
	5-4-12	✓	x	x	x	✓			
2014	11-24-14	✓	x	x	✓	x			
2015	5-12-15	✓	✓	✓	✓	✓			
	5-12-15	✓	✓	✓	x	✓			
	8-6-15	✓	✓	✓	x	✓			
2017	5-12-17	✓	x	✓	x	✓			
	6-20-17	✓	✓	✓	✓	✓			
	6-27-17	✓	✓	✓	✓	✓			
	7-4-17	✓	✓	✓	✓	✓			
	7-11-17	✓	✓	✓	✓	✓			
	7-18-17	✓	✓	✓	✓	✓			
	7-25-17	✓	✓	✓	✓	✓			
	8-3-17	✓	✓	✓	✓	✓	x	x	x



Retrospective Analysis (McCord *in prep*)

Year	Date	296.9473	346.9472	396.9409	406.9594	426.9657	340.9372	440.9302	540.9238
2011	11-4-11	✓	✓	✓	✓	✓	x	x	x
	1-26-12	✓	x	x	✓	✓	x	x	x
2012	2-1-12	✓	x				x	✓	x
	2-9-12	✓	✓				✓	x	x
	5-4-12	✓	x				x	x	x
	5-4-12	✓	x				x	x	x
2014	11-24-14	✓	x				x	x	x
2015	5-12-15	✓	✓				✓	✓	✓
	5-12-15	✓	✓				✓	✓	✓
	8-6-15	✓	✓				✓	✓	✓
2017	5-12-17	✓	x				✓	✓	✓
	6-20-17	✓	✓	✓	✓	✓	x	✓	✓
	6-27-17	✓	✓	✓	✓	✓	x	x	x
	7-4-17	✓	✓	✓	✓	✓	x	x	x
	7-11-17	✓	✓	✓	✓	✓	x	x	x
	7-18-17	✓	✓	✓	✓	✓	x	x	x
	7-25-17	✓	✓	✓	✓	✓	x	x	x
	8-3-17	✓	✓	✓	✓	✓	x	x	x



Formula: C₅H₂F₈O₆S
[M-H]⁻: 340.9372 Da



Questions?

Contact Information
strynar.mark@epa.gov

U.S. Environmental Protection Agency